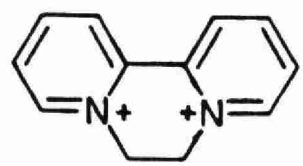
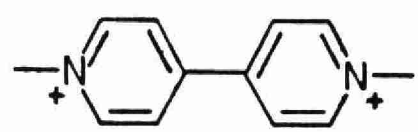
1997 Annual Report

RESEARCH AND DEVELOPMENT



diquat cation



paraquat cation

Laboratory Services Branch
Ontario Ministry of Environment

May, 1998

ISSN 1203-0104

1997 Annual Report

Research and Development

Laboratory Services Branch

May 1998

MAY 1998

Cette publication technique
n'est disponible qu'en anglais.

PIBS 2511e05

Overview

Since the previous report of this series, the Laboratory Services Branch continues to restructure and evolve away from routine testing towards support of core ministry functions and reference centre activities – a process we expect to be ongoing for a number of years.

This year's report includes information of activities other than our major R&D Projects. A new section has been added in which collaborative development projects with other government and private sector organizations are described. As part of our reference function, LSB has also initiated a seminar series. A synopsis of the 1997 seminar program also appears in this report.

Substantial progress was made in several areas of method development in 1997. A wide array of analytical technology including liquid chromatography-mass spectrometry, solid-phase extraction/micro-extraction, and HPLC/DIN/ICP/MS was applied to a wide range of challenging sample types from drinking water to compost, to improve the delivery of services to Laboratory Services Branch customers.

For further information on any of the projects described in this report, readers are directed to the Study Leader, or to the Author:

Dr. Ray Clement
Chair, Analytical Laboratory Services, R&D Committee
Ontario Ministry of Environment & Energy
Laboratory Services Branch
125 Resources Road
Etobicoke, Ontario M9P 3V6
Phone: 416-235-5906

Table of Contents

A. New Applications of Technology

Introduction

Solid Phase Extraction (SPE) is fast becoming the mainstream method of choice for the extraction of trace organic pollutants from aqueous sample types. Over the past few years, a few methods based on SPE have been brought on-line at the Laboratory Services Branch, and this year, four more methods have been investigated for suitability to the SPE technology. In addition to the obvious advantage of greatly reduced use of organic solvents for sample extraction, SPE methods generally require the use of less glassware and sample handling, and thus should provide high quality and improved sample turnaround for our customers.

Other technologies investigated include the use of liquid chromatography – (electrospray ionization) mass spectrometry (LC-MS), ion chromatography, and immunoassay. The LC-MS technology is still in its infancy as applied to environmental analysis, but after a decade of investigation electrospray ionization seems to be emerging as the LC-MS technique of choice for many environmental applications. The detection limits of some contaminants have been lowered enough to make LC-MS the technique of choice for some environmental applications that would prove difficult by other techniques. Immunoassay methods have also progressed substantially in recent years. Lowered detection limits for toxic organics such as the chlorinated dioxins and PCBs may soon bring immunoasssay-based methods into the mainstream of environmental analysis screening applications.

I. Determination of Diquat and Paraquat by Liquid Chromatography-(Electrospray Ionization) Mass Spectrometry [LC-(ESI)MS]

Study Leader:	Vince Taguchi, Mass Spectrometry/Volatiles Section
Study Team:	Steve Jenkins, Dave Wang, Patrick Crozier
Customer:	DWSP and drinking water customers (to meet PWQO), MOE Regional Pesticides Officers

Objective

To develop a simple, rapid and selective method for the determination of diquat and paraquat in water samples that meets the lower detection limits (compared to the ODWO – Ontario Drinking Water Objective) required by the Ontario Provincial Water Quality Objectives (PWQO), and that is applicable to a wide range of aqueous sample types.

Background

An alternative procedure to US EPA method 549.1 for diquat and paraquat was required using the specificity of mass spectrometry and the isotope dilution method of quantitation that automatically corrects for matrix recoveries. To simplify the sample preparation procedure, the analytes were adsorbed onto SPE cartridges without ion-pairing reagents and eluted with trifluoroacetic acid (TFA). Chromatography was developed on a microbore (1 mm i.d.) C1 column using methanol/water/TFA in the mobile phase. To provide additional selectivity in the detector, (electrospray ionization) mass spectrometry [(ESI)MS] was utilized. Because the TFA in the mobile phase caused suppression of ionization in the ESI process, propionic acid/isopropanol was added post-column to restore sensitivity. Interference problems needed to be solved. Performance data had to be obtained and the method had to be validated. Detection limits to meet the ODWO's of 70 µg/L for diquat and 10 µg/L for paraquat had been achieved but the PWQO for diquat of 0.5 µg/L had not yet been attained.

Results

Interference problems were solved by switching from SPE cartridges to ENVI-8 DSK SPE disks. Samples were concentrated using high purity air on a Zymark TurboVap. Chromatography was optimized on a microbore C1 (5 cm guard + 15 cm

analytical) column using 7% methanol/ 93% water/ 25 mM TFA at a flow rate of 40 µL/min. Propionic acid/methanol (3:1) was added post-column at a flow rate of 15 µL/min. ESI conditions were optimized to monitor diquat as the $[M^{2+}\text{-}H^{+}]$ ion (M^{2+} = dication) at m/z 183 and paraquat as the mono-trifluoroacetate ion pair $[M^{2+}/\ ^{-}OOCCF_3]$ at m/z 299. Quantitation was done using isotope dilution with d_4-diquat and d_8-paraquat and monitoring the corresponding ions $[M^{2+}\text{-}D^{+}]$ and $[M^{2+}/\ ^{-}OOCCF_3]$ at m/z 186 and m/z 307, respectively. Mass spectrometry was performed at low resolution (1,000 RP) to be compatible with quadrupole and ion trap mass spectrometers. Detection limits for diquat and paraquat were 0.1 µg/L and 0.2 µg/L respectively (based on the dication). Precision, accuracy and average recovery for diquat were 14%, ±6%, and 32%, respectively. The respective values for paraquat were 12%, ±3% and 66%. A batch of 24 samples, 9 method recovery (MR) samples, 2 spiked control (SC) samples and 1 method blank (MB) could be processed in 3 days. Because no breakthrough was observed for 500 mL samples on the ENVI-8 disks, it may be possible to lower the detection limits by using a larger sample volume. Studies showed that 25% of the losses could be attributed to the concentration and transfer steps. Diquat losses of 43% and paraquat losses of 9% were attributed to selective adsorption on the ENVI-8 disks with our disk elution solution. The LC-(ESI)MS method was compared to an existing LSB method utilizing ion-pairing on SPE cartridges followed by ion-pairing chromatography and detection by UV. Good correlation was obtained between the two methods when the LC-UV method results were corrected for recovery. Spiked matrix studies using the LC-(ESI)MS method on tap water, lake water, river water, ground water, and bog water showed that diquat and paraquat could be quantitated accurately even though the absolute recoveries were not known.

Current Status

Method development has been completed. The method E3405A is currently in use for routine sample analysis. The detection limits for diquat and paraquat of 0.1 µg/L and 0.2 µg/L, respectively (based on the dication) were adequate to meet the Ontario Drinking Water Objectives of 70 µg/L and 10 µg/L, respectively and the Ontario Provincial Water Quality Objective for diquat of 0.5 µg/L. A paper describing this work has been reviewed by the Journal of the American Society for Mass Spectrometry (ASMS) and is being revised for acceptance.

II. Determination of Cr^{6+} in Air Samples by Ion Chromatography

Study Leader:	M. Powell, Spectroscopy Section
Study Team:	D. Sturgis
Customer:	Standards Development Branch (R. Bell)

Objective

To develop a more sensitive and accurate technique to determine speciated chromium in impinger samples from a study site in southern Ontario.

Background

Bell and Hipfner[1] demonstrated that during a summer personal exposure survey in Hamilton, the geometric mean airborne Cr^{6+} concentrations measured outdoors and indoors at various homes scattered throughout the city was 0.55 ng/m^3 and 0.20 ng/m^3, respectively. They also found that there was no statistically significant relationship between the outdoor and indoor data sets, and that the majority of the airborne Cr^{6+} was in the inhalable fraction (i.e. less than 10μm [micron] in aerodynamic diameter). The analytical technique was based on a ion chromatography and was developed at the LSB by Chiu, from a State of California method for hexavalent chromium analysis[20]. However, with the increasing demand for lower detection limits, the technique has been modified. In order to obtain the necessary 50,000-fold increase in sensitivity, the Cr^{6+} analytical detection limit must now approach the 10 ppt (parts per trillion) level.

Results

A viable technique for the determination of Cr^{6+} in air samples has been developed. Modification of the Dionex 4500i system with the use of two injection valves and the Dionex AG4-SC column has separated the Cr^{6+} from the total chromium in the sample with good precision and sensitivity. A characterization and optimization study was conducted on the column to observe performance as well as effects from potential interferences. The detection limit obtained for the system was 25 ppt Cr^{6+}. Accuracy was established by comparing an in-house standard with standards from two alternate manufacturers.

Status

In future work the effects of chemical interference of the specific air matrix will be investigated by conducting a spiking study of real samples collected in the field. As well, a study on the effect of different sample loop sizes will be conducted to optimize the performance of the system in terms of sensitivity and column loading. Samples will be analyzed on an experimental basis starting in April 1998. At this point we will be able to do comparison tests with an alternate method. We expect to have a method development report written by the Fall, 1998.

References

1. Bell, R.W. and Hipfner, J.C. "Airborne Hexavalent Chromium in Southwestern Ontario", J. of the Air and Waste Management Association, August 1997, 47; 905-910 ISSN 1047-3289

2. State of California - Method 425, Determination of Total and Hexavalent Chromium Emissions from a Stationary Source, 1990

III. SPE Method for Diquat and Paraquat

Study Leader:	Lorna Grey
Study Team:	Ernie Chen, Paul Yang
Customer:	All Drinking Water Customers

Objectives

To develop a solid phase extraction method for the trace level testing of diquat and paraquat herbicides in drinking water and well water samples. This method is a lower cost but less sensitive method than the LC-(ESI)MS method described in Section I. The SPE method will be used for samples that do not require the lowest detection limits.

Background

The existing Solid Phase Extraction technique for paraquat and diquat involves the use of 6-mL disposable C8 extraction cartridges. The technique has evolved to the stage where it is rugged and reproducible. Factors affecting the recovery of analyte

using the SPE technique usually include the incomplete adsorption of the analyte on the SPE stationary phase during sample application (sample breakthrough), and premature or incomplete elution during the column washing or elution steps. The EPA method 549 SPE procedure for paraquat and diquat in environmental water samples has been modified the to ensure reproducible, high (75±25%) recoveries of paraquat and diquat.

Results

The SPE method for diquat and paraquat uses 6-mL (1 g), C8 SPE cartridges (Worldwide Monitoring, Mississauga, Ontario). This is different than the cartridge used in EPA Method 549 where a C18 cartridge is used. The cartridge was conditioned using a series of eight different solutions, including buffers at different pH values to achieve the best adsorbing ability possible. Details of these eight different solutions and usages are documented in LSB Method E3404. The water sample (200-mL) was extracted at a pH of 10.5 ± 0.2 (pH adjustment using 10% w/v NaOH or 10 % w/v HCl). The sample, along with its QC samples were filtered through the conditioned cartridges, at approximately 5 mL/min, under a 22 inches Hg vacuum (or less) supplied by a tap water aspirator or house vacuum. Diquat & paraquat were eluted from the cartridge using a buffered solution, and 100 µL of an ion-pair concentrate was added into each extract to facilitate separation and elution on the HPLC analytical column. The extract was diluted to 5 mL with more cartridge eluting buffer solution and was then analyzed by HPLC/Photodiode UV analysis. QC data obtained from the method are listed in the Table below.

	Paraquat			Diquat		
	Spiked. µg	Measured	Recovery, %	Spiked, µg	Measured	Recovery, %
1	12.5	11.00	88	12.5	13.25	106
2	12.5	10.13	81	12.5	12.50	100
3	12.5	10.13	81	12.5	12.13	97
4	12.5	11.88	95	12.5	13.25	106
5	12.5	9.00	72	12.5	9.75	78
6	12.5	9.75	78	12.5	9.63	77
7	12.5	9.13	73	12.5	9.63	77
8	12.5	8.38	67	12.5	9.50	76
9	12.5	9.00	72	12.5	10.00	80
10	12.5	9.13	73	12.5	10.25	82
11	12.5	9.75	78	12.5	10.99	87.9
Average		9.8	78		11	88
Standard Deviation		1.1	8.5		1.6	13
MDL	3.2			4.8		
W	0.7			1.1		

Current Status

Method development is complete. A performance evaluation study conducted using EPA and in-house standard has found the method performed flawlessly. A field study initiated by EMRB customers is expected to be completed by Summer, 1998.

IV. SPE Method for Carbamates and Phenyl Ureas

Study Leader:	Lorna Grey, Applied Chromatography Section
Study Team:	Ernie Chen, Paul Yang
Customer:	All Drinking/Surface Water Customers

Objectives

To develop solid phase extraction procedures for two methods: carbamate insecticides and phenyl urea herbicides in drinking waters, surface waters and ground waters, which will provide high quality data with increased analytical capacity and a reduction in the use of hazardous extraction solvents.

Background

Liquid/liquid extraction (LLE) has been the traditional technique for preparing various environmental water samples for instrumental analysis. LLE is typically not environmental friendly as it involves the use of large volumes of organic solvents some of which, like methylene chloride, are considered toxic. The Solid Phase Extraction (SPE) technique is similar to open column or low pressure liquid chromatography. It involves the use of small disposable extraction cartridges or disks which are filled or impregnated with a variety of sorbents. The technique has evolved to the stage where it is now rugged and reproducible. Factors affecting the recovery of analytes using the SPE technique usually include the incomplete adsorption of the analyte (sample breakthrough) to the SPE stationary phase during sample application; and premature or incomplete elution during the column washing or elution steps. The focus of this work has been to improve the SPE procedures to ensure sufficient recovery of most pesticide analytes. Method parameters to be investigated include the addition of buffers to the sample matrix prior to extraction and the fine tuning of sample volume via numerous QC samples.

Results

SPE method for Carbamates and Phenyl Ureas uses 6-mL (1 g) C18 cartridges. This is identical to the cartridge used in the organophosphorous (OP) method. In fact the extraction method is the same as for the OPs. The cartridge is cleaned with one cartridge volume of hexane. It is then conditioned with 5 mL methanol and 5 mL RO-deionized water. The sample is pre-treated with sodium thiosulphate as a preservative and 400 mL of sample are drawn through the cartridge at a rate of approximately 15 mL/min. After extraction the cartridge is dried by drawing air through for approximately one minute. The analytes are eluted from the cartridge using 10 mL ethyl acetate. The ethyl acetate is removed via rotary evaporation and the sample residue is reconstituted in 1 mL of acetonitrile. Before analysis by HPLC the extract is filtered using a 0.4 µm teflon filter. Carbamates are analysed by UV at 220 nm and phenyl ureas at 254 nm.

For carbamates, method recoveries for individual target compounds in fortified waters (reagent and real matrix) were between 72% and 100% with RSDs generally better than 10% (see Table). Extensive reproducibility studies have not yet been performed on the phenyl urea herbicides but results to date show recoveries 90 -110% for all analytes.

Carbamates SPE method - Instrument and Method Performance Summary

Compound	Instrument Performance				Method Performance (fortified reagent water)			
	Standard (ng/mL)	N**	Result (%)	RSD (%)	Spike (ng/L)	N	Recovery (%)	RSD (%)
Aldicarb	24000	6	101	1.6	9500	36	79	8
Propoxur	8000	6	100	0.7	4150	36	85	5
Carbofuran	8000	6	102	1.0	4150	36	87	5
Bendiocarb	8000	6	99	2.3	4550	36	95	12
Carbaryl	800	6	100	0.9	400	36	100	7
IPC	8000	6	99	1.5	2100	36	72	8
CIPC	8000	6	100	2.7	2000	36	85	7
Barban	8000	6	101	1.6	2200	36	87	7
Eptam	8000	6	101	3.1	4150	36	75	15
Diallate	8000	6	100	1.7	4150	36	77	8
Butylate	8000	6	100	1.9	4150	36	75	15
Triallate	8000	6	101	1.9	4100	36	85	5

**number of replicate determinations

Carbamates SPE - Method Detection Limits				
Compound	Method Detection Limits (fortified reagent water)			
	(ng/L)	N**	Recovery (%)	RSD (%)
Aldicarb	150	8	74	15
Propoxur	500	8	55	7
Carbofuran	500	8	71	9
Bendiocarb	500	8	69	9
Carbaryl	50	8	96	6
IPC	500	8	79	10
CIPC	500	8	79	10
Barban	1500	8	78	12
Eptam	1000	8	61	20
Diallate	1000	8	74	15
Butylate	1000	8	57	20
Triallate	500	8	73	12

**number of replicate determinations

Current Status

Method development is complete. Additional QC data will be obtained to verify this method's data comparability with data from the existing MOE-LSB phenyl urea method. Initial studies show that the method performance for these compounds is very good. The use of internal standards along with LC-MS for both carbamates and phenyl ureas will also be investigated. Reference standards will be used to evaluate the method before an internal LSB method audit is conducted. The SPE method has been validated against the LSB dichloromethane liquid/liquid extraction method using real-matrix spiked samples. The results are comparable to LSB/LLE method for carbamates; the phenyl urea method will be evaluated against the LLE method in the near future. Initial results are favourable.

V. SPE and GC/MS Analysis of Eleven Synthetic Pyrethroid Insecticides

Study Leader:	Larry Matchuk, Applied Chromatography Section
Study Team:	Barry Ali, Joe Fracassi, Paul Yang
Customer:	Operation Division Customers

Objectives

To develop a solid phase extraction (SPE) and GC/MS analytical method for the trace level testing of pyrethroid insecticides in water, vegetation, soil which will provide high quality data with increased analytical capacity and a reduction in the use of hazardous extraction solvents.

Background

The synthetic pyrethroid insecticides are analogs of natural pyrethroids known for centuries to have insecticidal activity. The most important natural pyrethroid, pyrethrum, is isolated from the heads of pyrethrum daisy (chrysanthemums). Synthetic pyrethroids, first developed in 1973, are more stable to light and possess a higher insecticidal activity, almost ten times that of most organophosphorus and carbamate insecticides. The stability and activity of the synthetic pyrethroids are reflected in their increased use during the last two decades on fruits, vegetables, corn, and especially cotton. The high activities of these chemicals allow relatively small amounts to be applied (about 100 grams/hectare). The environmental impacts of the synthetic pyrethroids, especially to ground and surface water, are still largely unknown.

Results

Based on a literature search, eleven pyrethroid isomers were selected for this development work. Using C18, SPE cartridges samples were prepared and analyzed using GC/MS. Several of these eleven compounds are chemical isomers, which makes quantitative analysis difficult. This was resolved by developing a GC temperature program that allowed baseline separation of the eleven pyrethroids. Method recoveries for individual target compounds in water sample were between 60% and 110%.

Current Status

This method is in its infancy. Standards have been prepared and analyzed to determine retention times and for the creation of library spectra. This procedure will be used as part of the LSB method E3404 for the non-target pesticide analysis. For routine water sample monitoring, we plan to determine and stabilize the extraction efficiencies using different solvents, SPE cartridges, and matrices.

VI. Aldehydes and Ketones in Ambient Air

Study Leader:	Mike Sage, Mass Spectrometry/Volatiles Section
Customer:	Standards and Development Branch

Objective

To develop a SPE and GC/MS method for the trace level testing of aldehydes and ketones in ambient air in support of the Standards Development Branch 3-year Standards Setting Plan.

Background

Monitoring indoor, industrial, and ambient air for formaldehyde and other aldehydes is challenging because of the specificity and sensitivity needed when sampling. Currently accepted methods include US EPA TO11 and US EPA IP-6A. These methods cite the use of dinitrophenylhydrazine (DNHP)-coated, silica-based, solid phase extraction cartridges for the collection and derivatization of these analytes. The DNPH reagent reacts to form the more stable hydrazone derivative which is recovered by solvent desorption of the adsorbent bed. The sample can then be analyzed by HPLC/UV.

Recently DNPH SPE devices, using the traditional syringe barrel configuration featuring low pressure drop for high sample flow rates, (up to 1.5 L/min when using a personal sampling pump) have been developed. These cartridges exhibit minimal background levels and provide sensitivity in the ppb concentration range.

A method employing GC/MS in place of HPLC/UV for the analysis of carbonyl hydrazone derivatives offers several advantages including convenience of use,

reductions in solvent consumption, shorter analysis times, and mass spectra data for positive identification of analytes.

Results

A preliminary GC/MS method has been developed for the analysis of formaldehyde and acetaldehyde. Hydrazone derivative standards at 15 ug/ml levels were analyzed in scan mode to determine optimum GC parameters, retention times and obtain mass spectra for the development of quantitative calibrations for both Scan and SIM modes. Instrumental analysis is done by fused silica capillary column GC - mass selective detector using external standard quantification techniques. Compound separations are done on a 30-meter HP-5MS column using an initial temperature of 150 C, 2 min. hold, ramp at 10 C/min to 300 C and 10 min hold. (Total time 27 min). Target compounds are identified by their retention times and presence of 3 characteristic ions in the correct relative abundances.

Compound	Retention Time	Ion Masses Monitored
2,4-DNPH formaldehyde	10.38	210.6
2,4-DNPH acetaldehyde	11.79	224.9

Current Status

Method development will now concentrate on sample collection, preparation and cleanup. The procedure is expected to entail the following steps; collection at 0.5 - 1.5 L/min on LpDNPH S10 cartridges (Sigma-Aldrich), solvent desorption with acetonitrile under vacuum and cleanup by passing eluant through a cation exchange resin (Dowex 50W-X8). The procedure will be evaluated for the following criteria; blank contamination levels, analyte recovery, precision, linearity, and detection limits.

Other carbonyl compounds may be evaluated for this method or alternatively by LSB method E3314 (VOC) depending on developments for this method currently being reviewed. Main concerns for this method's applicability relate to compound stability and moisture control in samples (possible loss of carbonyls when moisture is removed from the sample).

VII. Immunoassay Pre-Screening Technique for Dioxins/Furans in Fish

Study Leader :	Terry Kolic, Dioxins & Toxic Organics Section
Study Team :	Eric Reiner, Bob Harrison (Cape Technologies)
Customer :	Environmental Monitoring & Reporting Branch / Fish Contaminants

Objectives

To develop an immunoassay-based pre-screening technique for PCDD/Fs in biota samples to achieve detection limits comparable to GC/HRMS analysis.

Background

Immunoassay has been used in the field of clinical chemistry for the measurement of hormones, proteins, and drugs for the past 30 years. The movement towards development of environmental immunoassay tests for specific groups of compounds is a rapidly growing field. Immunoassay kits are available for various pesticides, PCBs and PAHs compounds. EPA has recognized and approved these test kits as field screening tools to aid in the remediation of various hazardous sites. To make an immunoassay test successful requires detection limits comparable to current available analytical methodology. This has been a major challenge for PCDD/Fs as these compounds are present in the environment at concentrations considerably lower (lower ppt range) in relation to their PCB and PAH counterparts. The World Health Organization (WHO) has identified 17 out of the 210 possible PCDD/Fs as toxic. These 17, even though they may be present at concentrations considerably lower than other PCDD/F congeners, contribute all of the toxicity. Each of the 17 congeners has been assigned its own toxicity equivalency factor (TEF) relative to the most toxic of the seventeen – 2,3,7,8-TCDD (TEF = 1). The current trend in PCDD/F reporting is in the form of total TEQ (toxic equivalent quantity) per sample, which is the sum of the concentrations of the 17 toxic PCDDs/PCDFs congener present in the sample multiplied by their respective TEFs. In order for immunoassay to be successful, the analysis must be selective towards the 17 toxic congeners which exhibit cross-reactivities similar to their associated TEFs. Immunoassay must also be able to achieve low detection limits as currently required for PCDD/F analysis.

If successful, only those samples where PCDD/PCDF concentrations exceed the MOE Sports Fishing Consumption Guideline of 10 ppt would require confirmation by GC/HR/MS or GC/MS/MS. This could decrease the amount of sample preparation time, sample size, turnaround times, and overall operating costs for PCDD/PCDF determinations, including a reduction in the amount of isotopically labeled analytical standards currently being consumed. A rapid screening method would also allow customers to examine a greater number of potential problem locations and to obtain rapid analytical turnaround for site remediation activities.

Results

Preliminary results, seen in Table I, indicate a considerable high bias for samples with results below 9 ppt (TEQ) as determined by GC/HRMS. For samples that were above 9 ppt the difference was a factor of two or less. There are two problems which could account for the positive bias of results at the lower concentration levels: first, the integrity of the conjugate solution during this preliminary study became suspect due to a yeast formation within the conjugate solution itself. It is possible the yeast may have hindered the conjugate from binding to the unoccupied antibody sites. This could account for the high values at the lower concentration range. Another potential problem could be the presence of 2,7,8-T_3CDD in the sample. It is known that in terms of cross-reactivity, this congener can contribute significantly to the total TEQ.

Current Status

A second immunoassay kit has been received with new sample tubes and solutions. Cape Technologies has improved the stability of the conjugate solution since the initial kit was distributed. Samples below 9 ppt will be re-examined to see if the problems still persists. Also, some of the original fish extracts should be re-analyzed by GC/HRMS specifically to determine if the 2,7,8 -T_3CDD congener is present in these samples. Currently the Dioxin Laboratory only monitors for congeners with degrees of chlorination between 4 and 8. Also, the various stages of sample cleanup will be investigated to determine whether all or part of the cleanup is necessary in order to carry out the immunoassay analysis.

Table 1. Comparison of EIA Analysis versus GC/HRMS Analysis in Biota Samples

Sample	Runs Per Sample	Average of EIA Runs TEQ(ppt)	GC/HRMS Analysis TEQs(ppt)	Relative Error Bias High (+) or Bias Low (-) (ppt)
K5604	3	13	2	5.5
L5134	2	9.6	2	3.8
L5131	4	29	3	8.7
K4064	2	7.5	4	0.9
K5602	3	17	5	2.4
L5133	2	55	7	6.9
K4062	2	10.6	9	0.2
K4061	2	14	14	0
L5135	4	39	20	1
K5605	3	33	27	0.2
L5132	4	52	66	-0.2

B. Methods Development

Introduction

This section reports on those method developments that involve new technology or procedures that require a research and development approach to their successful implementation. Trends affecting method development work include the determination of individual toxic PCB congeners, rather than a total PCB analysis, which is a priority need for several of our ministry customers. This is an outcome of the finding of toxicologists that individual PCB congeners have widely varying toxicities – analogous to the situation for the chlorinated dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs).

The speciation of organics, metals, and organometallics into individual rather than group concentrations, as is now widely accepted for the PCDDs and PCDFs, is an ongoing trend that is expected to continue. As our understanding of the toxicity of individual members of a compound class increases, the necessity of developing improved methods of separating close isomers from each other becomes apparent. Analytical methods must be able to distinguish between compounds that are highly toxic from those which are structurally similar but which have very low toxicity.

I. Hexane Micro-extraction Roller Methodology

Study Leader:	Marilyn Pitcher, Applied Chromatography Section
Study Team:	Stephanie Lemanik, Paul Yang
Customer:	All Drinking/Surface Water Customers

Objectives

To develop a microextraction and GC/ECD analytical method for the trace level testing of chlorinated organic pesticides and PCBs in drinking waters, surface waters and groundwaters which will provide high quality data with increased analytical capacity and a reduction in the use of hazardous extraction solvents.

Background

Solvent microextraction techniques offer several advantages over traditional liquid/liquid extraction methods. The reduction in the use of solvents cuts down the amount of hazardous wastes produced as well as reagent costs. Microextraction techniques significantly reduce the source of analyte loss and experimental error by reducing the need for sample clean-up and solvent reduction after extraction. The sample preparation time can be reduced from days to hours. Extraction is carried out in the original sample container which removes the need for glassware preparation. Therefore, the use of microextraction techniques has the potential to save chemical reagents, reduce labour and time, and therefore lower the test cost. Solvent microextraction has been applied to the analysis of pesticides by the USEPA, but their Method 505 does not encompass the target pesticides and meet detection limits required by current MOEE/LSB methods. The modification of USEPA Method 505 to reach ng/L (ppt) detection limits for all organochlorine target compounds in MOEE/LSB Method OWOC-E3120B was initiated.

Results

A routine hexane microextraction roller method has been developed to test for 35 chlorinated organic target compounds. The wet chemical preparation procedure, which is done in the original 1-L amber sample bottle, consists of surrogate, internal volume correction standard, and hexane (5 mL) addition to the 800 mL sample followed by sample rolling for 90 minutes and direct extract transfer to an autosampler vial. Instrumental analysis is done by dual fused silica capillary column GC - electron capture detection (GC/ECD) using internal standard quantification techniques.

Compound separations are done on 30 metre DB-1 and DB-1701 columns using a 55 minute single ramp oven program. Target compounds must be detected on both analytical columns and be within a specified quantification tolerance to be considered present in the extract. Method recoveries for individual target compounds, including PCBs, in fortified waters (reagent and real matrix) were between 79% and 117% with RSDs generally better than 5% (see Table).

Current Status

Method development was completed as of May 1997. The method (LSB Method # E3400A) was accredited by CAEAL in June 1997. The microextraction method has been validated against the LSB dichloromethane liquid/liquid extraction method using real-matrix spiked samples, NIST reference materials and CAEAL audit samples.

Table 1: **Within-Run Performance Summary of Microextraction Method**

Compound	Spike (ng/L)	N	Average Recovery (%)	RSD (%)
hexachloroethane	25	8	79	3
1,3,5-trichlorobenzene	125	8	97	2
1,2,4-trichlorobenzene	125	8	93	4
1,2,3-trichlorobenzene	125	8	98	2
hexachloro-1,3-butadiene	25	8	84	4
2,4,5-trichlorotoluene	125	8	101	5
2,3,6-trichlorotoluene	125	8	100	3
1,2,3,5-tetrachlorobenzene	25	8	95	2
1,2,4,5-tetrachlorobenzene	25	8	107	2
1,2,3,4-tetrachlorobenzene	25	8	105	3
α,2,6-trichlorotoluene	125	8	99	1
pentachlorobenzene	25	8	117	2
hexachlorobenzene	25	8	99	3
heptachlor	25	8	98	2
aldrin	25	8	88	2
p,p'-DDE	125	8	94	2
α-BHC	25	8	98	1
trifluralin	125	8	109	3
γ-BHC (lindane)	25	8	96	2
α-chlordane	50	8	105	3
γ-chlordane	50	8	102	3
oxychlordane	50	8	103	3
o,p'-DDT	125	8	98	3
p,p-'DDD	125	8	91	2

p,p'-DDT	125	8	91	5
methoxychlor	125	8	93	5
heptachlor epoxide	25	8	100	3
endosulfan I	50	8	101	3
dieldrin	50	8	106	2
endrin	100	8	94	2
endosulfan II	100	8	105	2
endosulfan cyclic sulphate	100	8	100	4
mirex	125	8	93	5
octachlorostyrene	25	8	85	3
polychlorinated biphenyl (PCBs)	100	8	87	7
toxaphene	125	9	95	7

Recovery (%) = ([spike result]/[expected result]) x 100

II. Method for Isomer-Specific Dioxin-like PCB Congener Analysis

Study Leader:	K. MacPherson, Dioxins & Toxic Organics Section
Study Team:	T.Kolic, V.Khurana
Customer:	Environmental Monitoring and Reporting Branch (Fish Contaminants & Surface Water)

Objectives

To develop a quantitative and selective method using isotope dilution mass spectrometry for the isomer-specific determination of the Dioxin-like PCB congeners identified by The World Health Organization (WHO).

Background

The chlorinated dioxins (PCDDs) and furans (PCDFs) are members of a class of toxic chemicals known collectively as endocrine disruptors. Regulatory limits for PCDDs/PCDFs have been established based on a Toxicity Equivalency (TEQ) approach, in which the concentrations of individual PCDDs and PCDFs are multiplied

by a factor based on their relative toxicity to 2,3,7,8-TCDD, the most toxic compound of this class. Regulations can then be based on the total TEQ concentration.

Since the mid 1990s this TEQ approach has been modified to include other endocrine disruptor compounds. Of special concern are certain Dioxin-like PCBs. Current estimates of these PCBs compared with 2,3,7,8-TCDD suggest that these substances may increase our exposure, up to one order of magnitude, as assessed by TEQ. The World Health Organization (WHO) originally designated TEQ Factors (TEFs) for 13 of the 209 possible PCBs. As a result of a recent TEF re-assessment study carried out by WHO, some modifications have been made to the original PCB congener designations as well as their associated TEFs. Because various biological organisms have different enzyme systems which affect the uptake, metabolism and elimination of endocrine-disrupting chemicals, an alternate TEF scheme has been proposed for Dioxins/Furans and Dioxin-like PCBs in fish and avian wildlife (see table I).

Initial reports in the literature suggested that 5 of the "toxic 13" PCB congeners could be analyzed using the current MOE Dioxin/Furan method with minor modifications. Preliminary results indicated that major modifications to the cleanup scheme would be required to isolate and detect congener 118. It became evident that the major method modifications required to recover PCB-118 would enable the remaining eight dioxin-like congeners to be determined using the modified LSB method.

Results

Isotopically labelled standards purchased for development of a quantitative method to analyse for five of the PCB congeners revealed quantitative discrepancies between suppliers. A third standard was obtained from an independent source to complete the validation of these in-house standards and provide the data quality objectives currently achieved for MOE Dioxin/Furan determinations. Participation in an *International Intercalibration Study on PCDDs, PCDFs and planar PCBs in a Fly Ash Extract* reported excellent performance by our laboratory for the analysis of the three most toxic PCBs.

The addition of eight PCB congeners to the target list required the acquisition and validation of additional isotopically labeled PCB standards. The standard series was modelled after the calibration series currently used for quantitation of Dioxins and Furans. All instrumental conditions have been optimized and all parameters set up for the analysis of the "Dioxin-like" congeners originally identified by the WHO as well as for the two recently added congeners. WHO added PCBs #81 and #167 to the list of compounds with designated TEFs in September 1997.

Current Status

Two additional PCB standards, congeners #81 and #167 have been purchased. Our in-house inventory now includes all the PCBs identified by WHO as Dioxin-like. The continual addition of congeners over the last two years has made it difficult to maintain validated up-to-date standards and to complete the method development of the "Dioxin-like" PCB method. The Dioxin lab plans to analyse for the complete set of congeners currently designated by WHO as Dioxin-like as well as for the original list of congeners and PCB#209.

Table I - WHO TEF Reassessment results

Congener	Toxic Equivalency Factor (TEF)		
	Humans & Mammals	Fish	Birds
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PCDD	1	1	1
1,2,3,4,7,8-HxCDD	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.01	0.1
1,2,3,4,6,7,8,-HpCDD	0.01	0.001	<0.001
OCDD	0.0001		
2,3,7,8-TCDF	0.1	0.05	1
1,2,3,7,8-PCDF	0.05	0.05	0.1
2,3,4,7,8-PCDF	0.5	0.5	1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0001	0.0001	0.0001

PCB Congener	Toxic Equivalency Factor (TEF)		
	Humans & Mammals	Fish	Birds
3,4,4',5-TCB (81)	0.0001	0.0005	0.1
3,3',4,4'-TCB (77)	0.0001	0.0001	0.05
3,3'4,4',5-PCB (126)	0.1	0.005	0.1
3,3',4,4',5,5'-HxCB (169)	0.01	0	0.001
2,3,3',4,4'-PCB (105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PCB (114)	0.0005	<0.000005	0.0001
2,3',4,4',5-PCB (118)	0.0001	<0.000005	0
2',3,4,4',5-PCB (123)	0.0001	<0.000005	0
2,3,3',4,4',5-HxCB (156)	0.0005	<0.000005	0.0001
2,3,3',4,4',5'-HxCB (157)	0.0005	<0.000005	0.0001
2,3',4,4',5,5'-HxCB (167)	0.00001	<0.000005	0
2,3,3',4,4',5,5'-HpCB (189)	0.0001	<0.000005	0

** Shaded areas represent TEFs that have changed as a result of WHO TEF reassessment (Sept.'97)

III. Congener-Specific Method for PCBs

Study Leader:	Rob Brunato, Dioxins & Toxic Organics Section
Study Team:	Rob Brunato, Eric Reiner, Tony Chen
Customer:	EMRB (Fish Contaminants, Surface Water), Standards Development Branch (PhytoToxicology, Aquatic Toxicology) and Region Operations Division

Objective

To develop a new analytical method to improve the non-isomer-specific analysis of low level PCB congener groups in sediment and biota and to reduce analysis time.

Background

PCBs were used in electrical transformers, caulking, paints, inks, insecticides and dielectric fluids. The use of PCBs has been banned since the late 1970s. Technical mixtures of PCBs, called Aroclors, have distinct congener patterns that are dependant on the degree of chlorination. Through the years, most environmental samples have become aged or weathered and the PCB patterns observed in environmental samples are no longer representative of the original Aroclor mixture. Congener specific data gives a more accurate indication of the state, toxicity and levels of PCBs in the sample and environment.

Results

Two analytical systems were evaluated for this study: a Hewlett Packard 5890 series II GC with dual ECD detectors and two analytical columns [60 meter DB5; 25mm i.d., 0.25 micron film thickness and a 60 meter DB1701 0.25mm i.d., 0.25 micron film thickness]; and a Hewlett Packard 6890 Fast GC with ECD detector. Four columns will be evaluated on the HP 6890: DB5-10 meter, 0.1 mm i.d., 0.4 micron film thickness; DB5 20 meter, 0.1 mm i.d., 0.1 micron film thickness; DB5 40 meter 0.18mm i.d., 0.18 micron film thickness; and a DB5 60 meter, 0.25 mm i.d., 0.25 micron film thickness.

The 58 target PCB congeners to be analyzed, shown in Table 1, were chosen based on their environmental occurrence, abundance, and toxicity.

Table1: PCB Congeners to be Monitored

Monochlorobiphenyls:	1,3
Dichlorobiphenyls:	4,8,10 and 15
Trichlorobiphenyls:	18,19,22,28,33,37
Tetrachlorobiphenyls:	44,49,52,54,70,74,77,81
Pentachlorobiphenyls:	87,95,99,101,104,105,110,114,118,119,123,126
Hexachlorobiphenyls:	128,138,149,151,153,155,156,157,158,167,168,169
Heptachlorobiphenyls:	170,171,177,178,180,183,187,188,189,191
Octachlorobiphenyls:	194,199,201,202,205
Nonachlorobiphenyls:	206,208
Decachlorobiphenyls:	209

All Biota samples were prepared using method E3136A (The Determination of

PCBs, OCs and CBs in Fish, Clams and Mussels by GC/ECD). All sediment samples were prepared using method E3270A (The Determination of PCBs, OCs and CBs in Soil and Sediments by GC/ECD).

Instrument conditions for both the HP 5890 series II and HP 6890 Fast GC have been determined for the analysis of PCB congeners. A linearity study for the HP 5890 series II has been completed with linearity greater than 4 orders of magnitude. Certified reference materials have been analysed. Results are in good agreement with target values for most congeners. Further studies will be completed to identify 3 or 4 interfering compounds.

Current Status

Precision and reproducibility study is still to be evaluated on HP 5890 series II and on HP 6890 Fast GC. The PCB congener method is still to be evaluated against existing LSB method E3136A (PCBs in Biota) and method E3270A (PCBs in Soil and Sediments) using spiked matrix samples. More certified reference materials will be analysed in order to determine the source of the interfering compounds and how they can be removed.

IV. Multiplex Analysis for Organophosphorus, Carbamates, Phenyl Ureas

Study Leader:	Lorna Grey, Applied Chromatography Section
Study Team:	Ernie Chen, Paul Yang
Customer:	All Drinking/Surface Water Customers

Objectives

To develop a single extraction/LC method for the trace level testing of carbamate (CAR), phenyl urea (PUH) and organophosphorus (OP) pesticides in drinking waters, surface waters and ground waters to replace three existing individual methods for these compound classes.

Background

Carbamate, phenyl urea, and organophosphorus pesticides are currently being analyzed by the Applied Chromatography Section using three separate sample preparation and HPLC/UV methods. All these compounds are amenable to extraction via one SPE or one liquid/liquid extraction method as has been shown by various ACS method development projects. OPs and CAR are analyzed via HPLC at 220 nm, PUHs are analyzed at 254 nm. CAR and PUH use a 25 cm; 4.6 mm; 5 µm C18 reversed phase LC analytical column. OPs use a Resolve C18 column. This column has a low percentage of normal phase capabilities. An effort is being made to incorporate the three methods into one by using a bench top LC/MS system. By replacing the three methods by one, considerable savings in cost and improved efficiency can be realized.

Results

The simultaneous extraction of CAR and PUHs from fortified reagent water samples has been attempted. The results are consistent with those of individual SPE extractions for these classes of compounds. The extracts have been analysed by a HPLC/UV multi wavelength detection at 220 and 254 nm and also by HPLC/DAD at 220 and 254 nm using both a 15 cm and 25 cm reversed phase C18 LC analytical column. Again, the results compare favourably to the analyses of the separate analyte groups. The chromatography still has to be optimised to resolve the elution of the carbamates (carbofuran, bendiocarb and propoxur) from the phenyl ureas (fluormethuron and chlortoluron). An attempt has not yet been made to add OPs to the analytical run. The analytical results so far are encouraging and progress is being made towards the optimization of the LC analysis.

Current Status

Method development is continuing. The next step will be to analyse the samples using LC-MS using the electrospray sample delivery technique. This approach will minimize the necessity of fully resolving each analyte peak as the MS will provide identification of the individual unresolved peaks. Several LC analytical columns which, according to literature reviews and the results of preliminary evaluations, should have the potential of better separating the analytes from the three classes of compounds. The research team is currently analysing spiked raw, surface and drinking water samples for CAR, PUH and OP using the multiresidue SPE method.

V. Determination of Taste and Odour Compounds in Water Using Ambersorb 572 and High Resolution Mass Spectrometry

Study Leader:	J-P.F.P. Palmentier, Mass Spectrometry/Volatiles Section
Study Team:	Vince Taguchi
Customer:	DWSP and drinking water customers (including Metro Works); MOE Regional Offices; County Regional Laboratories

Objective

To develop a general GC-HRMS method for taste and odour causing compounds by modifying the existing method for geosmin and 2-methylisoborneol (2-MIB) to incorporate 4 additional compounds: 2,3,6-trichloroanisole, 2,4,6-trichloroanisole, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine.

Background

Taste and odour problems occur seasonally in drinking and surface waters around North America. Six compounds have been identified as being responsible for imparting earthy, musty taste and odour qualities to water, food and soil. These include geosmin, 2-methylisoborneol (2-MIB), 2,3,6-trichloroanisole (TCA), 2,4,6-TCA, 2-isopropyl-3-methoxypyrazine (IPMP) and 2-isobutyl-3-methoxypyrazine (IBMP). Geosmin and 2-MIB are semi-volatile metabolites of actinomycetes and blue-green algae and are most often responsible for taste and odour events. IPMP is another taste and odour causing compound resulting from actinomycetes activity in water and soil. IBMP has been found in food. 2,3,6-TCA and 2,4,6-TCA are formed from reactions occurring during chlorination of drinking water or are discharged in Kraft pulp mill effluent. Human threshold odour concentrations for these six compounds have been reported as 10 ng/L for geosmin, 29 ng/L for 2-MIB, 7-30 ng/L for 2,3,6-TCA, 2-5 ng/L for 2,4,6-TCA and 2 ng/L for both IPMP and IBMP. The taste and odour causing compounds, geosmin and 2-methylisoborneol (2-MIB), are analyzed at the ministry using a granular adsorbent, Ambersorb 572, and isotope dilution high resolution mass spectrometry (HRMS)(7,000 RP). This method is highly productive and provides rapid (<48 hr) turnaround times.

Results

The GC temperature program from the geosmin/2-MIB method afforded good separation of all the components except for 2,3,6-TCA and geosmin. By introducing 2 temperature ramp programs, chromatographic conditions were eventually optimized for their separation. Five voltage switching scan functions, with their appropriate magnet settings were implemented to maximize sensitivity for all analytes. To quantitate the 2,3,6-TCA and 2,4,6-TCA, d_5-2,4,6-trichloroanisole was obtained and the molecular ions 209.9406 and 214.9720, respectively were monitored. For IPMP and IBMP, the base peaks m/z 137.0715 [$M-CH_3$] and m/z 124.0637 [$M-C_3H_6$], respectively were chosen for maximum sensitivity. 2-Methoxypyrazine (2-MP) was tested as an internal standard for IPMP and IBMP. However, recovery of the 2-MP was poor and 2-MP chromatographed poorly with significant peak tailing. No interferences have been observed in samples previously analyzed for geosmin and 2-MIB.

Current Status

The compounds, 2-sec-butyl-3-methoxypyrazine and 2-ethyl-3-methoxypyrazine, will be assessed for suitability as internal standards for the IPMP and IBMP. The availability and cost of a deuterated methoxypyrazine will be investigated. Initial experiments indicate that detection limits in the 1-2 ng/L range are possible at 7,000 RP for the 4 additional compounds.

C. Collaborative Projects

For many years, LSB staff have been participating in collaborative R&D projects with other researchers in the private, academic, and government sectors. These collaborations usually take the form of instrument or method evaluations, or the provision of analytical services for specialized sample sets. LSB assistance is also provided where a minor effort is required on the part of LSB staff for provision of analytical services in support of Government of Ontario goals. The collaborative and assistance projects described in this section provide examples of reference centre type work provided by the Laboratory Services Branch.

I. Evaluation of the GCQ Ion Trap Mass Spectrometer

LSB Study Team: Patrick Crozier, Mass Spectrometry/Volatiles Section
Collaboration with: Jeff Plomley, Thermo Instruments Canada Inc.

The Thermo Instruments GCQ, an external source ion trap mass spectrometer, was evaluated for its MS and MS/MS capabilities. PAHs were analyzed for sensitivity comparisons with the Varian Saturn 2000 ion trap and the HP5973 MSD single quadrupole mass spectrometer. In the full scan MS mode, the ion traps were more sensitive than the MSD by several orders of magnitude. In the SIM MS mode, the MSD was within an order of magnitude of the ion traps. In the MS/MS mode, sensitivity enhancement of the $[M\text{-}2H]^{+\cdot}$ ion was observed with resonant collision induced dissociation (CID). This led to an MS/MS method for the determination of PAHs, where detection limits of ~1 ng/L were achieved for 17 PAHs after sample concentration with SPE cartridges.

II Identification of sulfur-containing PAHs by GC-HRMS

LSB Study Team:	Vince Taguchi, Mass Spectrometry/Volatiles Section
Collaboration with:	Brian McCarry and Laurie Allan, McMaster University

McMaster University does not have the capability to do GC-HRMS. This capability was needed to identify sulphur-containing PAH detected in Hamilton air samples. Therefore, accurate mass determinations were done using full scans on the LSB VG ZAB-2F GC-HRMS system. Empirical formulae consistent with the sulfur-containing PAHs.were obtained. To obtain better detection limits, a GC-(SIM)HRMS experiment was set up to monitor these thia-arenes.

III Confirmation of digitoxin by (electrospray ionization) mass spectrometry [(ESI)MS]

LSB Study Team:	Vince Taguchi, Steve Jenkins, Patrick Crozier, Mass Spectrometry/Volatiles Section
Collaboration with:	Dave Riley, Centre of Forensic Sciences

The Centre of Forensic Sciences originally requested confirmation of digitoxin by solid probe MS. This was done on the VG Trio-2; however, the required detection limit of 5 ng could not be met. Subsequently, confirmation by (ESI)MS gave 3 ions characteristic of digitoxin: $M+H^+$ at m/z 765, $M+Na^+$ at m/z 787 and digitoxin acetate at m/z 806. Chromatography was developed on a C1 microbore column. Detection limits were <5 ng using SIM. Confirmations for RIA are now possible.

IV. Determination of anti-fungal agents and mycotoxins by (ESI)MS

LSB Study Team:	Vince Taguchi, Steve Jenkins, Patrick Crozier, Mass Spectrometry/Volatiles Section
Collaboration with:	Aimin Li, Ministry of Health

The anti-fungal agents terbinafine and itraconazole were analyzed by (ESI)MS to demonstrate the usefulness of the technique to MOH. Mycotoxins were also analyzed by (ESI)MS. Rubratoxin exhibited a characteristic ion at m/z 583 $[M + 2CH_3OH + H^+]$, ochratoxin A gave a $[M+H^+]$ ion at m/z 404, and penicillic acid gave ions at m/z 171 $[M+H^+]$ and m/z 153 $[M + H^+ - H_2O]$. Patulin showed a weak ion at m/z 261 $[M + acetate + 2\ CH_3OH]$. (ESI)MS was shown to be a promising technique for these compounds. Further studies would require determination of detection limits, establishment of sample

concentration techniques, and developing compatible chromatography conditions.

V. Evaluation of Portable GC/MS Instrumentation

LSB Study Team:	Mike Sage, Mass Spectrometry/Volatiles Section
Collaboration with:	Inficon Ltd.

The Hapsite is a field-portable GC-MS instrument capable of on-site analysis of field samples for organics such as volatile organic compounds (VOCs). Use of this field-portable system would result in significant reductions of sample analysis reporting times, and can significantly reduce costs in activities such as site cleanup. Because no sample preconcentration is performed, detection limits are 1-2 orders of magnitude worse than are generally obtained by shipping samples to a remote laboratory. In a two-week laboratory evaluation, single compound detection limits in the high part-per-billion range were observed, consistent with manufacturer's claims. The precisions observed for individual compound determinations were in the 10% range.

VI. Quality Assurance for New Zealand National Dioxin Survey

LSB Study Team:	Eric Reiner, Karen MacPherson, Terry Kolic, Tereza Gobran, Vin Khurana, Dioxin & Toxic Organics Section
Collaboration with:	Simon Buckland, New Zealand Ministry for the Environment

Public awareness in New Zealand of pollution from toxic chemicals such as the chlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and PCBs is high. As the pulp & paper industry is one of the largest in New Zealand, major concerns exist about possible pollution from PCDDs and PCDFs. A national survey was instituted to test rural and major urban areas across the country for PCDDs, PCDFs, PCBs, and other chemicals of concern, such as pesticides. Routine analytical work was contracted to the private sector, but a second laboratory was needed to analyze replicate samples for quality control purposes. The LSB Dioxin laboratory was asked to assist because of their international reputation in PCDD/PCDF analysis. The final report from this study has not yet been released, but excellent agreement was obtained between the LSB data and private laboratory for replicate sample analyses.

D. Education & Training

As the Laboratory Services Branch develops as a reference centre, education and training programs will become an important means to achieve the Branch goal of ensuring a province-wide analytical laboratory system that delivers readily available and acceptable quality testing in Ontario. During 1997, staff of the Branch led two educational workshops in support of this goal.

I. Course on Inductively Coupled Plasma Source Atomic Spectroscopy

On August 18-21, 1997, a course on Inductively Coupled Plasma Source Atomic Spectroscopy was conducted by MOE – Laboratory Services Branch staff in partnership with Brock University and the Perkin-Elmer Corporation. The course was initiated by David Boomer (LSB) and Professor Ian Brindle (Brock University), and was principally designed by David Boomer and Mark Powell of MOE. Other instructors were Scott McGeorge (Transition Technologies), Roger McLaughlin (Brock University), Cameron McCleod (Center for Analytical Chemistry, Sheffield, UK), and Cammy Raposo (MOE-LSB). Designed as an intermediate-level course for practitioners, 16 registrants spent four days in a combination of lectures and hands-on instrumentation training. The course attendees, who were principally industry practitioners, learned how to produce quality information by gaining practical knowledge that will allow them to run complex methods in the most suitable manner.

II. Workshop on Presence–Absence (P–A) Test Kit

On October 29, 1997, Garry Horsnell of MOE-LSB conducted a workshop on the correct procedures for using commercial P–A test kits for detecting faecal indicator bacteria. In attendance were about 60 Ontario water treatment plant (WTP) operators and MOE abatement staff. On-site P–A testing is necessary at WTPs, but the application of proper techniques is necessary to ensure that commercial kits give reliable results. The 1-day workshop covered the use of aseptic techniques, sample collection and transport, bacteriological testing methods, and the use of four commercially-available P–A kits. The advantages and limitations of the P–A method and of the use of the commercial test kits were explained. How to ensure the highest quality results was emphasized.

E. LSB Seminar Series

Seminars are an important vehicle for communicating new developments in the analytical science field. For three years, the Laboratory Services Branch has been running an analytical seminar series. Selected seminar speakers are leaders in some field related to environmental analysis, or have special expertise in a specific area of interest to the LSB R&D community. Speakers are drawn from academia, industry, other government agencies, or from within LSB. The following seminars were held at the Branch during 1997:

I. Biosensors for Applications to Environmental Problems
Ulrich Krull, University of Toronto – Erindale College

Professor Ulrich Krull visited LSB on January 23 to describe how biosensors can be used to investigate difficult environmental analysis applications. The goal of biosensor development is to create devices that can be used to selectively and rapidly detect and measure organic substances in solution, even when the sample contains mixtures of organic substances.

In the seminar, current biosensor technology in terms of device design and construction was described. Analytical capability and limitations for detection of substances of environmental interest such as pesticides and herbicides were considered, and new directions associated with the detection of organisms such as E. coli and cryptosporidia by rapid analysis of DNA and RNA were highlighted.

II. Environmental Immunoassay: From Pesticides to Dioxin
Robert O. Harrison, Cape Technologies, Scarborough, Maine, USA

On Thursday, May 1, Dr. Harrison briefly reviewed the principles and history of envoronmental immunoassay, especially the development of commercial kits. A new immunoassay for PCDD/Fs was described which offers significant performance advantages over any previous dioxin immunoassay. A multi-laboratory collaborative effort now in progress for evaluation of kit performance and the development of sample preparation methods was outlined. LSB staff of the Dioxin Unit are currently in a collaborative project with Dr. Harrison to evaluate the performance of this new test kit for PCDDs/PCDFs in fish (see Section A, project VII).

III. Use of High Speed GC/HRMS for Assessing Human Exposure to Endocrine Disrupting Chemicals
Donald G. Patterson, Centers for Disease Control & Prevention, Atlanta, USA

Dr. Patterson presented his seminar on Thursday, May 1. He described recent reports that have presented evidence that certain synthetic chemicals as environmental pollutants are capable of disrupting animal hormone systems. Many of these chemicals are found in human tissues. To meet increased analytical demands for these chemicals, the CDC developed a number of high-speed single and multidimensional techniques, as well as methods compatible with direct measurements in human samples with high sample throughput and low detection limits (S:N of 15 for 350 attograms 2,3,7,8-TCDD). High speed GC allowed many more samples to be analyzed during a working day compared to conventional GC, and therefore saved time and cost.

IV. Thia-arenes as Source Trackers
Brian McCarry, Chemistry Department, McMaster University

Thia-arenes are sulfur-containing polycyclic aromatic hydrocarbons (PAH) that are present in environmental samples that contain PAH. Thia-arenes are present at levels 10-100 fold lower in abundance than PAH. The profile of thia-arene isomers derived from petrogenic sources is quite different from the profile of isomers derived from coals. Professor McCarry and his group have developed an analytical methodology which exploits this difference and has allowed them to differentiate between coal-based emissions and diesel-based emissions in air particulate, sediments and biota.

Another project of interest MOE is the development of an analytical method for the quantitation of carbon black in ambient air. At present no method exists to detect and quantify carbon black. Professor McCarry has identified a thia-arene compound adsorbed to many carbon blacks that can be used as a tracer for this material. He also discussed the results from examining air particulate material collected in Hamilton upwind and downwind of a carbon black plant. This seminar took place Thursday, December 4.

Publications and Presentations - 1997
Analytical Laboratory Services

A. Publications

1. J. Plomley and P. Crozier. *Qualifying Ion Enhancement in the Trace Level Analysis of PAHs in Drinking water by GC-Ion Trap Mass Spectrometry*. Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, Florida, June 1-5, 1997; p. 934.

2. C.Tashiro, D.W.Potter, B.R.Yeo, B.J.Sharratt, C.J.Harrison, F.J.Campbell, B.G.Chittim, E.J.Reiner, K.MacPherson, and T.Kolic. *Congener Specific PCB Analysis by HRGC/HRMS: Reference Materials*. Proceedings of the 17th International Symposium on Chlorinated Dioxins and Related Compounds **31,** 56-60.

3. Sylvia Cussion. *Industry Intercomparison for Solvent Extractables (ATG 25): DCM vs Hexane*. Ministry of Environment & Energy, Laboratory Services Branch Report September 22, **1997**.

4. Ray E. Clement, Lawrence H. Keith, and K.W. Michael Siu, editors: *Reference Materials for Environmental Analysis*. Lewis Publishers, Boca Raton, Florida **1997**, 278 pp.

5. Ministry of Environment and & Energy, Laboratory Services Branch. *Guidance Document for Sample Collection and the use of Commercial Presence-Absence (P-A) Tests for the Bacteriological Analysis of Drinking Water*. Toronto, Ontario, January **1997**, 27 pp.

6. R. Lega, G. Ladwig, O. Meresz, R.E. Clement, G. Crawford, R. Salemi, and Y. Jones. *Quantitative Determination of Organic Priority Pollutants in Sewage Sludge by GC/MS. Chemosphere* **1997**, *8*, 1705-1712.

7. L. Birnbaum, R. Clement, H. Fiedler, O. Hutzinger, E. Reiner, and S. Safe, Editors: *Chlorinated Dioxins, PCB and Related Compounds 1995*, Proceedings of the International Conference on Chlorinated Dioxins and Related Compounds, Edmonton, Alberta, August 1995. *Chemosphere* **1997**, V. 34 (5-7).

8. M. Powell. *Standard Operating Procedures (SOP)*. Proceedings of the 28th Annual Conference, Canadian Mineral Analysts; Peterborough, Ontario, Sept. 16-19, 1996, pp. 248-252.

9. Ronald W. Bell and Jerold C. Hipfner. *Airborne Hexavalent Chromium in Southwestern Ontario. J. Air & Waste Manage. Assoc.* **1997**, *47*, 905-910.

10. Ray E. Clement,Paul W. Yang, and Carolyn J. Koester. *Environmental Analysis. Anal. Chem.* **1997**, *69*, 251R-287R.

11. Eric J. Reiner and Ray E. Clement. *From Stack Testing to Final Report: Getting it Right.* Proceedings of the Air & Waste Management Association's 90[th] Annual Meeting and Exhibition, **1997**, paper 97-FA162.02, 8pp.

12. Ray E. Clement. *Environmental Science Education: Critical Skills Missing and How to Get Them.* Proceedings of the Air & Waste Management Association's 90[th] Annual Meeting and Exhibition, **1997**, paper 97-A215, 5pp.

13. Ray Clement and Eric Reiner. *Femtograms or Phantomgrams? An Analytical View of the Organochlorine Issue. Canadian Chemical News* **1997** (September), 26-27.

14. M. Splendore, R.E. March, E.J. Reiner, D.S. Waddell and K.A. MacPherson. *A Comparison of Three Mass Spectrometric Methods for the Determination of Dioxins.* Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, Florida, June 1-5, 1997; p. 193.

B. Presentations

1. J.B. Plomley and P.W. Crozier. *The Analysis of PAHs in Drinking Water: Achieving Future Detection Limit Guidelines using a Quadrupole Ion Trap* Joint 29th Eastern Canada Pesticide and Environmental Contaminants Workshop/Northeast Regional Section AOAC International 16th Annual Meeting, Ottawa Ontario, May 12-15, 1997.

2. J.B. Plomley and P.W. Crozier. *Ion Trap Sensitivity for PAH Analysis by Selected Ion Monitoring is Enhanced by the Collisionally Induced Dissociation of the Molecular Cation during Isolation of the [M-2H] Confirmatory Species*; 32nd Annual Western Canada Trace Organic Residue Analyst's Workshop, Winnepeg, Manitoba, May 4-7, 1997.

3. Ijaz Ahmad. *Analytical Methods for Sewer Use By-Law Application*, workshop - Central Ontario Municipality Engineering Laboratories Group, Toronto, Ontario, June 24, 1997.

4. R.E. Clement. *Environmental Analysis in the Real World*, Invited Seminar Presented to Chemistry Department, Queen's University, November 26, 1997, Kingston, Ontario.

5. R.E. Clement. *Environmental Monitoring in the Real World*, Invited Lecture Presented to Senior Environmental Studies Class, York University, October 31, 1997, Toronto, Ontario.

6. R.E. Clement. *How to Get A Science Job*, Invited Talk Presented at Chemical Institute of Canada, Toronto Section, Annual Awards Night, October 29, 1997, University of Toronto.

7. R.E. Clement. *Introduction to Spectroscopy*, Lecture Presented to Undergraduate Students, Ryerson University, September 16, 1997, Toronto, Ontario.

8. R.E. Clement. *Environmental Resources Guides of A&WMA*, Invited Presentation at Environmental Education Workshop, July 22, 1997, Toronto, Ontario.

9. R.E. Clement. *Environmental Science Education: Critical Skills Missing and How to Get Them.* Presented at the Air & Waste Management Association's 90th Annual Meeting and Exhibition, June 10, 1997, Toronto, Ontario.

10. E.J. Reiner and R.E. Clement. *From Stack Testing to Final Report: Getting it Right.* Presented at the Air & Waste Management Association's 90th Annual Meeting and Exhibition, June 13, 1997, Toronto, Ontario.

11. R.E. Clement. *Life After Graduation: Essential Job Search Skills*, Invited Lecture Presented to Career Services Dept. Course, Wilfred Laurier University, March 13, 1997, Waterloo, Ontario.

12. R.E. Clement. *Air Toxics: The Dioxin Story*, Invited Seminar Presented to Chemistry Department, York University, March 13, 1997, Toronto.